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COMPLETE SPECIFICATION

Electrodialysis of Chloride-containing Liquids

We, NEDERLANDSE CENTRALE ORGANISATIE VOOR TOEGEPAST-NATUURWETENSCHAPPELIJK ONDERZOEK, of 12 Koningskade, The Hague, The Netherlands, a Body Corporate organised under the Laws of the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the purification of chloride-containing liquids by means of an electrodialytic process carried out in apparatus having a closed anode rinsing liquid circuit in which the anode rinsing liquid is continuously recycled during the process, a permeable membrane being present between the liquid to be purified and the liquid which is in contact with the anode. In order to decrease the resistance of the cell, thin membranes are preferred in most cases and the distance between the anode membrane and the anode is kept small, this distance preferably being less than 10 mm and even less than 5 mm.

When the liquid to be electrodialysed contains chlorine ions, these chlorine ions penetrate the anode membrane under the influence of the electromotive force and are discharged at the anode with the formation of chlorine, which partly dissolves in the liquid and partly escapes in a gaseous state.

As the distance from membrane to anode becomes smaller (distances of about 1 mm have been used), the membrane is found to be attacked to an ever increasing degree and metals used in the construction of the circuit are corroded. When electrodialysis is used for the removal of chlorides from albumen solutions or from other liquids containing organic material easily attacked by chlorine, a membrane consisting for example of cellophane, collodion or parchment, still has a sufficiently long life to be considered suitable for technical use, provided that the electrodialysis is carried out under suitable conditions. In these cases it is preferable that the pH of the dialysate be not too high, e.g., not above 9, as it was found that the attack becomes stronger at higher pH values.

The chlorine concentration in the anode liquid may be maintained low by adding a substance yielding sulphite ions, as described in United Kingdom Specification No. 679,338.

When electrodialysis is applied to the complete or partial removal of chlorine from water, such as sea water or brackish water, to obtain water suitable for use as distilled water, as drinking water for the purpose of irrigation in agriculture and horticulture, the degree to which the anode membrane is attacked is so serious, however, that all electrodialysis processes have hitherto failed in practice (c.f. Prof. Aten Chem. Weekblad 1928, *25*, page 211, 648; Billiter, Specification No. 431,695).

Specially developed membranes (leather, processed filter cloth) have also proved unsuitable for technical application. Ceramic diaphragms have the drawback of a very high resistance, even if they are made as thin as possible, while in this latter case they are moreover exceedingly fragile.

It is the main object of the invention to provide process and apparatus for the removal in a simple way of chlorine formed at the anode on electrodialyzing chloride-containing liquids while continuously recycling an anode rinsing liquid in a closed anode rinsing liquid circuit:

It has now been found that the attack on the membranes by chlorine, dissolved in the circulating anode rinsing liquid, is substantially reduced or practically obviated if a flow of a medium which is in the gaseous state at the working temperature of the anode rinsing liquid is passed through the anode rinsing liquid.

Accordingly the present invention provides a process for the prevention of corrosion in a closed anode rinsing liquid circuit

in which the anode rinsing liquid is continuously recycled during electrodialysis of chloride-containing liquids, wherein a flow of a medium which is in the gaseous state at the working temperature of the anode rinsing liquid is passed through the anode rinsing liquid. The present invention also provides an apparatus for electrodialyzing chloride-containing liquids comprising alternate electrode and electrodialysis cells separated by permeable membranes, a closed anode rinsing liquid circuit and means for continuously recycling the anode rinsing liquid through the said circuit; the said apparatus being provided with means for preventing by the above process, corrosion in the said closed anode liquid rinsing circuit, namely means for passing a medium which is in the gaseous state at the working temperature of the anode rinsing liquid through the anode rinsing liquid and means for separating the said medium from the anode rinsing liquid.

It was found that it was not necessary to pass gas or vapour through in such quantities that the partial pressure of chlorine was maintained at a very low level. In some cases it was even sufficient to blow through the anode liquid a volume of gas or vapour a few times greater than the volume of chlorine gas developed, and in many cases a volume of 10-30 times that of the chlorine gas was sufficient.

Instead of passing the flow of gas or vapour along the anode (the disadvantage of which is that the effective surface of the membrane is decreased by the gas bubbles on the surface), in many cases it is sufficient to decrease the chlorine content of the anode rinsing liquid to a considerable extent by blowing a quantity of air or another gas through the liquid after it has left the cell. After this process the anode rinsing liquid is used again. The rinsing liquid may even be circulated by means of an air lift, the air of the air lift at the same time decreasing the chlorine content.

In principle the air may be passed through the circulating rinsing liquid either before or after the liquid has left the anode compartment.

Experience has shown that attack of the membranes in the liquid in the anode chamber was substantially decreased by reducing the content of chlorine to less than 10 mg. of active chlorine per litre.

When cellophane membranes are used, the cellulose is presumably oxidised by chlorine with formation of carboxyl groups. The degree of attack by chlorine may be observed by causing a solution of methylene blue to act upon the oxidised membrane, the methylene blue being absorbed in accordance with the degree of oxidation. In this way it is possible to establish the circumstances under which the membrane is attacked. In this way it was found that on treatment outside the cell with a solution of chlorine in acidified water, having a pH of e.g., about 2, such as is to be found in the anode rinsing liquid, nearly no coloration of the cellophane of the membrane takes place.

Thus other phenomena occur during the process of electrodialysis, which cannot be exclusively explained by a chemical reaction between chlorine and membrane.

If only a reduced quantity of air is used, the rinsing liquid coming from the rinsing compartment sometimes contains so much active chlorine that the anode membrane is still attacked. It was found that this attack could be wholly prevented by the removal of the remaining chlorine, which can be attained by the addition of sulphurous acid or salts thereof, either to the rinsing liquid or, in some cases, by addition to the dialysate.

Other gases or vapours such as nitrogen, carbon monoxide, carbon dioxide, gaseous or vaporous hydrocarbons, which do not react with the components of the anode rinsing liquid, may be used instead of air.

EXAMPLE 1.

Very much active chlorine is formed in the anode compartment during the electrodialytic desalting of water (brackish water or sea water) in a three-compartment apparatus, all the compartments of which are fed with the same water.

A solution containing about 1,000 mg. of Cl-per litre was continuously desalted with a current of about 50 Amp. in an apparatus having a membrane surface of 0.27 square metres per membrane. The anode rinsing liquid was continuously recycled through a closed circuit in which was included an expansion vessel, that is to say a vessel filled only partly with the rinsing liquid so as to allow of expansion of the liquid and escape from the liquid of gas formed at the anodes. The anode rinsing liquid circulated with a velocity of 1,000 litres/hour; 30 litres of water were supplied per hour. The content of active chlorine in the anode rinsing liquid increased to a value of about 1,100 mg/litre during this process.

The expansion vessel was now replaced by a vessel having a height of 70 cm. The anode rinsing liquid coming from the anode compartment was sprayed by means of a nozzle into the top of this vessel. 20 cubic metres of air per hour were blown in at the bottom of the vessel, which was about half filled with rinsing liquid. The air passes first through the liquid and thereupon through the descending drops sprayed from the nozzle, and subsequently escapes from the top of the vessel. When the above-described process was worked in combination with this aeration, the chlorine content of

the anode rinsing liquid did not exceed about 10 mg. per litre.

EXAMPLE II.

Concentrated whey is electrodialysed in a three-chamber apparatus with an anode membrane of 0.280 square metres surface with a current of 500 Amp., during which process the liquid of each of the three compartments is circulated individually.

0.2 N Na_2SO_4 and 0.05 N H_2SO_4 (in a total quantity of about 35 1/hour) are regularly supplied to the anode rinsing liquid, fresh concentrated whey is also regularly supplied to the concentrated whey in the middle compartment, and the desalted product is constantly carried off, so that a continuous process is obtained. Working as described above, the Cl-content of the anode rinsing liquid varies between about 2,000 and 3,500 mg/litre; the content of active chlorine carries between 700 and 1,000 mg/litre.

When 24 litres of air per minute are passed through anode compartment, the content of active chlorine decreases to 70-100 mg/litre; when 80 litres of air per minute are passed through, this content falls to 30-40 mg/litre.

If, moreover, after the de-aeration, SO_2 (either as such, or as solution of sodium sulphite in water) is supplied to the liquid, it is possible to maintain the content of active chlorine below 10 mg/litre.

The content of active chloride in the anode rinsing liquid can also be maintained at a low level by addition of sodium sulphite to the dialysate.

What we claim is:—

1. A process for the prevention of corrosion in a closed anode rinsing liquid circuit in which the anode rinsing liquid is continuously recycled during electrodialysis of chloride-containing liquids, wherein a flow of a medium which is in the gaseous state at the working temperature of the anode rinsing liquid is passed through the anode rinsing liquid.

2. A process as claimed in Claim 1, wherein the gaseous medium is also used for the circulation of the anode rinsing liquid.

3. A process as claimed in Claim 1 or 2, wherein a flow of air is passed through the anode rinsing liquid.

4. A process as claimed in any of the preceding claims, wherein the pH of the dialysate is constantly maintained below 7.

5. A process as claimed in any of the preceding claims, wherein, in addition, a small quantity of sulphur dioxide or of a sulphite is added to the dialysate.

6. A process for the prevention of corrosion in the anode rinsing liquid circuit during electrodialysis of chloride-containing liquids, substantially as described with reference to either of the Examples.

7. An apparatus for electrodialyzing chloride-containing liquids comprising alternate electrode and electrodialysis cells separated by permeable membranes, a closed anode rinsing liquid circuit and means for continuously recycling the anode rinsing liquid through the said circuit; the said apparatus being provided with means for preventing, by the process claimed in Claim 1, corrosion in the said closed anode liquid rinsing circuit, namely means for passing a medium which is in the gaseous state at the working temperature of the anode rinsing liquid through the anode rinsing liquid and means for separating the said medium from the anode rinsing liquid.

8. An apparatus as claimed in Claim 7, including an air lift pump for recycling the anode rinsing liquid.

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